

Quantum-classical lifetimes of Rydberg molecules

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Abstract. A remarkable property of Rydberg atoms is the possibility to create molecules formed by one highly excited atom and another atom in the ground state. The first realisation of such a Rydberg molecule has opened an active field of physical investigations, and showed that its basic properties can be described within a simple model regarding the ground state atom as a small perturber that is bound by a low-energy scattering process with the Rydberg electron [C. H. Greene *et al* , Phys. Rev. Lett., 85: 2458 (2000)]. Besides the good agreement between theory and the experiment concerning the vibrational states of the molecule, the experimental observations yield the astonishing feature that the lifetime of the molecule is clearly reduced as compared to the bare Rydberg atom [B. Butscher *et al* , J. Phys. B: At. Mol. Opt. Phys. 44, 184004 (2011)]. With focus on this yet unexplained observation, we investigate in this paper the vibrational ground state of the molecule in a quantum-classical framework. We show that the Rydberg wave function is continuously detuned by the presence of the moving ground state atom and that the timescale on which the detuning significantly exceeds the natural linewidth is in good agreement with the observed reduced lifetimes of the Rydberg molecule.

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1. Introduction

The field of Rydberg atoms which possess a highly excited valence electron has been established decades ago, and it is still an active one today (see Ref. [1] for a recent review and references therein). One reason for the interest in such highly excited atoms is the fact that important properties of these atoms in general scale universally with powers of the principal quantum number n . For highly excited atoms ($n \gg 1$) this leads, e.g., to extremely large extensions up to the size of a virus, huge polarizabilities as well as van der Waals-coefficients and long lifetimes, making these atoms ideal candidates for applications in quantum simulations or quantum computing [2].

Besides these remarkable properties, Rydberg atoms are also of great interest, because they are able to form very weakly bound molecules together with a second atom in the ground state [3]. Such Rydberg molecules were first realised in 2009 with rubidium atoms [4], and the experiment showed that the basic properties of the molecule can be well described within a simple model [3]. Regarding the ground state atom as a small perturber which is polarised by the Rydberg electron the interaction can be described theoretically by a low-energy scattering process. If the respective scattering length is negative, the interaction leads, within a mean-field approximation, to a binding and oscillatory molecular potential, and the theoretical predictions agree very well with the measured vibrational spectra of the molecules [4].

However, a remarkable and not yet fully explained property of the Rydberg molecules is that surprisingly they exhibit mean lifetimes τ which are clearly reduced when compared to the bare atomic Rydberg state [4, 5, 6]. Butscher *et al* [7] found that the atomic background gas has a significant influence on the lifetime due to inter-particle collisions. For the decay rate $\gamma = 1/\tau$ they found a linear dependence $\gamma = \gamma_0 + c\mathcal{N}$ on the background gas density \mathcal{N} which can be explained using classical scattering theory. However, regarding the vibrational ground state in the limit $\mathcal{N} \rightarrow 0$, the background atoms cannot play a role in the reduction of the lifetimes. Nevertheless, the measurements indicate a ground state's lifetime of $\tau_0 = 47.6 \mu\text{s}$ while the bare atoms have a lifetime of $\tau_{\text{atom}} = 62.5 \mu\text{s}$. In this zero density limit, the system only consists of three parts, namely the Rydberg core, the Rydberg electron and the ground state atom, so, obviously, the reduced lifetime must be caused by the ground state atom somehow perturbing the Rydberg wave function.

In order to uncover the reason for this difference in the lifetimes of about 25%, a convenient approach in molecular physics would be to evaluate the non-adiabatic energy terms which govern the energy transfer between nuclear and electronical motion. These terms couple a particular Rydberg state with the continuum of dissociation of a lower-lying one and, thus, allow for a predissociation process under the change of the electronic state. In addition to spontaneous photon emission and blackbody induced radiation, such a process may further shorten the lifetime of the molecule. However, a quantitative evaluation of the corresponding decay rate requires the determination of the non-adiabatic coupling terms which is a difficult task.

As an alternative, we therefore pursue a different approach in this paper to investigate the decay mechanism initiated by the ground state atom in a Rydberg molecule. That is based on a quantum-classical description of the Rydberg molecule [8] which allows us to take into account the effect of the ground state atom onto the Rydberg atom beyond the usual treatment of a static disturber. In previous work [9, 10] the perturbation of the Rydberg state has been considered at a fixed position \mathbf{R} of the non-moving ground state atom. In this paper, we introduce a model in which the moving of the ground state atom plays an important role, viz. the Rydberg state is continuously detuned due to a transfer of kinetic energy from the ground state atom to the Rydberg state. A detuning comparable or larger than the natural linewidth of the Rydberg state will enhance the transition to a lower Rydberg state resulting in the decay of the molecule by either spontaneous photon emission or predissociation. As we will show below, the time when the detuning significantly exceeds the natural linewidth of the vibrational ground state agrees very well with the lifetime in the zero density limit. Moreover, we find that the detuning becomes smaller with increasing principal quantum number, so that the experimentally measured tendency of longer lifetimes with increasing n is also in accordance with our treatment.

Our paper is organised as follows: In Sec. 2, we give a brief review of the quantum mechanical description [3] as well as of the quantum-classical treatment [8]. In Sec. 3, we apply the latter approach to a rubidium Rydberg molecule in the s-state. The detuning is discussed in detail for the vibrational ground state of a molecule with $n = 35$ and comparisons with the corresponding experiment are made. Moreover, we demonstrate the effect of the detuning for different experimentally accessible principal quantum numbers $n = 33 - 41$.

2. Theory

In this section, we review the quantum mechanical description of the scattering process between the Rydberg electron and the ground state atom as well as the quantum-classical treatment. Both approaches are discussed briefly and we refer the reader to Refs. [3, 8] for details.

2.1. Molecular potential of Rydberg molecules

The binding mechanism of the Rydberg molecule is based on the polarisation of the ground state atom under the influence of the Rydberg electron. This interaction can be described theoretically using a Fermi type pseudopotential [11]

$$V(\mathbf{r}, \mathbf{R}) = 2\pi a_s(k) \delta(\mathbf{r} - \mathbf{R}), \quad (1)$$

where \mathbf{r} and \mathbf{R} denote the positions of the Rydberg electron and the ground state atom, respectively. The whole information on the scattering process is given, here, by the s-wave scattering length $a_s(k)$. It depends on the wave vector k of the Rydberg electron

and can be expressed by its first-order approximation [12] $a_s(k) = a_{s,0} + \frac{\pi}{3}\alpha k + \mathcal{O}(k^2)$ with $a_{s,0} = -16.05$ a.u. being the zero-energy scattering length and $\alpha = 319$ the polarizability of the rubidium target [4, 13, 14]. Greene *et al* [3] showed that, in a mean-field approximation, this contact interaction leads to the molecular potential

$$V_s(\mathbf{R}) = 2\pi a_s(k) |\psi_{\text{Ry}}(\mathbf{R})|^2, \quad (2)$$

where $\psi_{\text{Ry}}(\mathbf{R})$ is the value of the Rydberg wave function at the position \mathbf{R} of the ground state atom. In the case of $a_s(k) < 0$, we obtain an attractive interaction which allows for bound states. Fig. 1a shows the resulting molecular potential (2) for the above mentioned physical parameters (solid line) and indicates the energy and internuclear distance of the vibrational ground state (horizontal red line) which is located in the outermost potential minimum.

Note that significant modifications of this potential are caused for small internuclear separations when also p-wave scattering is taken into account by the additional term $V_p(\mathbf{R}) = 6\pi a_p^3 |\nabla \psi_{\text{Ry}}(\mathbf{R})|^2$, with the p-wave scattering length $a_p = -21.15$ a.u. [13] (see dashed line in Fig. 1a). This correction is important for the formation of Rydberg molecules at energies $E \lesssim 0$ [8]. However, in this paper we will solely consider the vibrational ground state of the molecule which is located in the outermost potential minimum, and, as can be seen in Fig. 1a, the p-wave contribution can be neglected there.

2.2. Energy detuning of the Rydberg state in the quantum-classical framework

One consequence of the mean-field approach of Greene *et al* [3] is the fact that Eq. (2) associates a *fixed* position \mathbf{R} of the ground state atom with the potential energy $V_s(\mathbf{R})$. Physically this is equivalent to the assumption of a vanishing ratio of masses of the two scattering partners, i.e. $m_e/m_{\text{Rb}} = 0$. Although the ground state atom is, by far, heavier than the electron ($m_e/m_{\text{Rb}} \approx 6 \times 10^{-6}$ for rubidium), this assumption is not strictly fulfilled. Considering the single scattering events leading to the bound molecule, we must, therefore, expect a momentum and, with it, also an energy transfer between the ground state atom and the Rydberg electron occurring with each orbit of the latter.

In order to take into account such effects, we will investigate the system in a quantum-classical way [8]. We describe the positions and the motion of, both, the Rydberg electron as well as the ground state atom as that of point particles while the scattering process between these two is treated fully quantum mechanically. Because of the high excitation of the Rydberg atom ($n \gg 1$), correspondence principle allows us to treat the motion of the Rydberg electron in terms of the classical trajectories whose angular momentum L and energy E will be quantised semiclassically:

$$L = l + \frac{1}{2}, \quad E = \frac{\mathbf{p}^2}{2} - \frac{1}{r} = -\frac{1}{2n^2}. \quad (3)$$

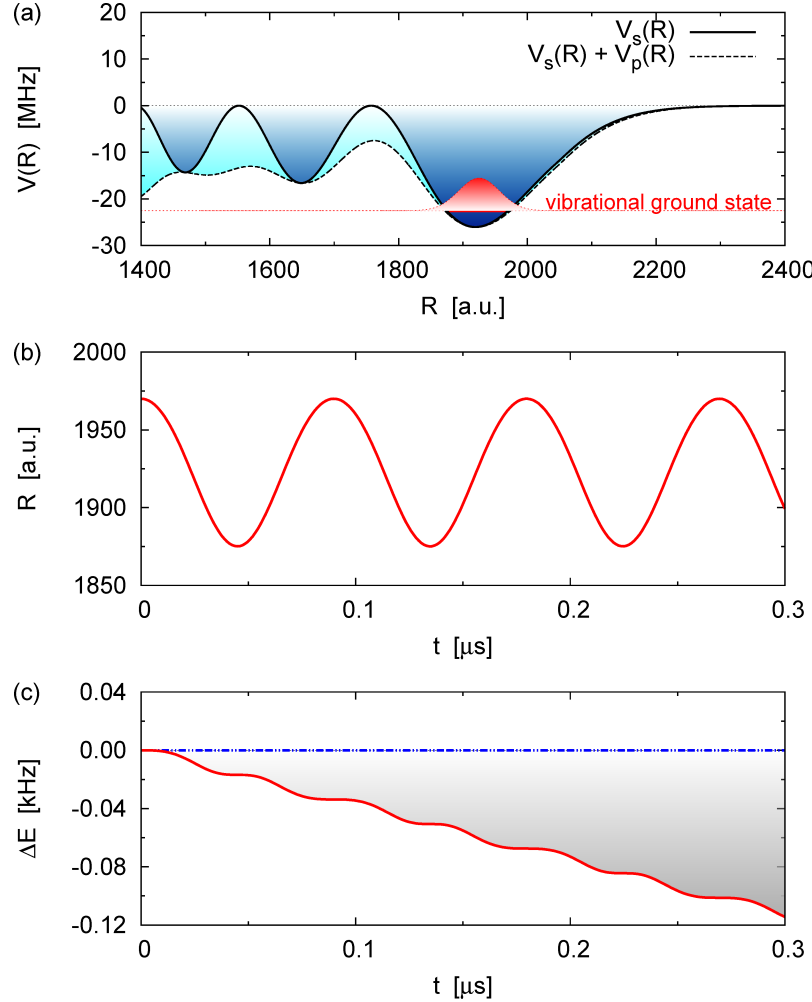


Figure 1. (a) Molecular potential of a rubidium Rydberg molecule in the $n = 35$ s-state. Shown are, both, the potential $V_s(\mathbf{R})$ taking into account only the s-wave contribution (solid line) and for comparison the potential $V_s(\mathbf{R}) + V_p(\mathbf{R})$ including p-wave scattering (dashed line). At internuclear separations $R \approx 1875 - 1970$ a.u. where the vibrational ground state (horizontal red line) is located the p-wave contribution can be neglected. (b) Oscillation of a point particle in the molecular potential $V_s(\mathbf{R})$ at the energy of the vibrational ground state. (c) Energy detuning ΔE of the ground state atom: Within the conservative potential resulting from the mean-field approximation, there is no energy detuning (blue dashed-dotted line), however, energy is transferred to the Rydberg electron with each oscillation in the quantum-classical treatment (red solid line). Note that, because of energy conservation, the energy of the Rydberg state is increased by $-\Delta E$.

Here, $n = 1, 2, 3, \dots$ and $l = 0, 1, 2, \dots$ denote the principal and azimuthal quantum numbers, \mathbf{p} is the momentum of the Rydberg electron and $r = |\mathbf{r}|$ is its distance from the core.

Since the interaction between the Rydberg electron and the ground state atom is of contact-like type, we only need to consider those orbits which include the position \mathbf{R} of the ground state atom. Considering a Rydberg atom in an s-state ($l = m = 0$), there

remain four ellipses which we *locally* approximate by a superposition of plane waves

$$\psi_{\text{Ry}}(\mathbf{r}) \approx \sum_{i=1}^4 \psi_{\text{pw}}^{(i)}(\mathbf{r}) = \sum_{i=1}^4 A^{(i)} \exp(i\mathbf{p}^{(i)}\mathbf{r}). \quad (4)$$

In order to determine their amplitudes $A^{(i)}$, we require this superposition to fulfil

$$\psi_{\text{pw}}|_{\mathbf{r}=\mathbf{R}} = \psi_{\text{Ry}}|_{\mathbf{r}=\mathbf{R}}, \quad (5a)$$

$$\partial_{\rho,z}\psi_{\text{pw}}|_{\mathbf{r}=\mathbf{R}} = \partial_{\rho,z}\psi_{\text{Ry}}|_{\mathbf{r}=\mathbf{R}}, \quad (5b)$$

$$\partial_{\rho,z}^2\psi_{\text{pw}}|_{\mathbf{r}=\mathbf{R}} \approx \partial_{\rho,z}^2\psi_{\text{Ry}}|_{\mathbf{r}=\mathbf{R}}, \quad (5c)$$

i.e. to reproduce the value of the Rydberg wave function and its derivatives identically on the one hand, and to approximately reproduce the second derivatives on the other. Here, Eq. (5c) has to be understood in the sense that the norm of the difference of both sides be minimal. Altogether, Eqs. (5a)–(5c) provide the best possible approximation of the Rydberg wave function by the four plane waves.

With the knowledge of the plane waves, the scattering interactions can be calculated straightforwardly: Each of them represents a Rydberg electron with momentum $\mathbf{p}_{\text{in}}^{(i)} = m_e \mathbf{v}_e^{(i)}$ which is scattered to an outgoing wave

$$\psi_{\text{out}}^{(i)} \sim \frac{\exp(ip_{\text{out}}^{(i)}|\mathbf{r} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{R}|}. \quad (6)$$

Because of the spherically symmetric angle distribution the total momentum of the outgoing s-wave is $\mathbf{p}_{\text{out}}^{(i)} = 0$, and the momentum transfer Δp is connected with an energy transfer ΔE between the ground state atom and the Rydberg electron.

Describing successive collisions of $N^{(i)}$ electrons by a current density $\mathbf{j}^{(i)} = n_e^{(i)} \mathbf{v}_e^{(i)}$ ($n_e^{(i)} = |A^{(i)}|^2$ is the electron density on the i -th Kepler ellipse), the total momentum transfer $\Delta \mathbf{p}^{(i)} = N^{(i)} m_e \mathbf{v}_e^{(i)}$ over time can be associated with a classical force

$$\mathbf{F}^{(i)} = \Delta \mathbf{p}^{(i)} / \Delta t = n_e^{(i)} m_e \sigma |\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}}|^2 \hat{\mathbf{e}}_{(\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}})} \quad (7)$$

acting on the ground state atom. Here, $\sigma = 4\pi a_s^2(k)$ is the total scattering cross-section and $\hat{\mathbf{e}}_{(\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}})}$ is the unit vector in the direction of $\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}}$. The energy detuning over time of the ground state atom induced by Eq. (7) is consequently given by

$$\frac{dE}{dt} = \sum_{i=1}^4 \mathbf{F}^{(i)} \cdot \mathbf{v}_{\text{Rb}} = m_e \sigma \sum_{i=1}^4 n_e^{(i)} |\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}}|^2 \left[\hat{\mathbf{e}}_{(\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}})} \cdot \mathbf{v}_{\text{Rb}} \right], \quad (8)$$

where the sum $i = 1, \dots, 4$ takes into account all four contributing Kepler ellipses. Note that, because of energy conservation, the detuning of the Rydberg state is given by the negative of Eq. (8), and that the value of dE/dt is significantly changing with time because of the vibrational motion of the ground state atom. Thus, an appropriate mean energy detuning can be obtained by averaging Eq. (8) over one oscillation,

$$\langle dE/dt \rangle = \int_0^T dt' [dE/dt'], \quad (9)$$

where T is the periode of the vibrational oscillation. Moreover, since the energy detuning is proportional to the velocity of the ground state atom, $dE/dt \propto \mathbf{v}_{\text{Rb}}$, the main contribution is obtained when the ground state atom is fast and there will be no contribution when it does not move, i.e. at the turning points of the oscillation.

Depending on whether the two scattering partners fly in the same ($\mathbf{v}_e^{(i)} \cdot \mathbf{v}_{\text{Rb}} > 0$) or in the opposite ($\mathbf{v}_e^{(i)} \cdot \mathbf{v}_{\text{Rb}} < 0$) direction, the respective contributions to Eq. (8) differ and the latter is always dominant because in this case the term $|\mathbf{v}_e^{(i)} - \mathbf{v}_{\text{Rb}}|$ is larger. Therefore, the net effect of Eq. (8) is always an energy transfer from the ground state atom to the Rydberg electron, i.e. the Rydberg state is permanently detuned.

The energy detuning is quantum mechanically not strictly forbidden because the vibrational ground state of the Rydberg molecule is metastable and has some finite lifetime τ . This directly implies a finite width in frequency space $\Delta\nu = (2\pi\tau)^{-1}$ which is, for typical lifetimes of a few tens of μs , on the order of several kHz, and, thus, small compared to the level spacing of the Rydberg atom. Note that an exponential decrease of the ground state's population leads to a Lorentzian form

$$I(\nu) \sim \frac{1}{(\nu - \nu_0)^2 + (\Delta\nu/2)^2} \quad (10)$$

of the spectroscopic line. Consequently, detunings $\nu \neq \nu_0$ are allowed, but reduce the intensity $I(\nu)$ and, for very low intensities, one expects a change of the electronic state (e.g. $n \rightarrow n - 1$). Because the intensity $I(\nu)$ decreases continuously with increasing difference of the frequency $\nu - \nu_0$ and the tail of the Lorentzian is extended infinitely, a clear threshold for the frequency ν which distinguishes the quantum mechanically allowed region ν (where we do not expect a change of the electronic state) from the forbidden one (where we do expect the electronic state to change) does, therefore, not exist. Therefore, we estimate these regimes in the following way: A detuning which is smaller than the natural linewidth, $|\nu - \nu_0| \lesssim \Delta\nu$, will be surely allowed, while much larger detunings $|\nu - \nu_0| \gg \Delta\nu$ are quantum mechanically forbidden so that we expect a detuning on the order of a few natural linewidths, $|\nu - \nu_0| \sim \Delta\nu$, to determine the threshold where the transition of the electronic state will set in resulting in the decay of the molecule by spontaneous photon emission or predissociation.

3. Results and discussion

In this section, we demonstrate the effect of the energy detuning in Eq. (8) for ^{87}Rb Rydberg atoms in the spherically symmetric s-state. At first, we will discuss the detuning of the vibrational ground state in general, then compare the results with the experimentally measured lifetimes and, finally, investigate the effect of different principal quantum numbers n on the time development of the detuning. Note that all calculations presented take into account a quantum defect correction of $\delta = 3$ [15].

3.1. Detuning of the molecular states

The Rydberg molecule is quantum mechanically described by the corresponding wave function ψ_{Ry} . The vibrational ground state of the molecule is located in the outermost potential minimum of the oscillatory molecular potential and does not extend into one of the neighbouring wells, since their minima are energetically higher than the ground state (see Fig. 1a). This wave function describes the probability density of the ground state atom, which oscillates in this outermost potential well, to be found at a specific internuclear distance.

The classical analogue is a point particle oscillating in this potential well between two turning points R_{min} and R_{max} . Fig. 1b shows this oscillation of the ground state atom with a binding energy of $E_0 = -22.5174$ MHz [16] for a Rydberg molecule in which the Rydberg atom is excited to the $n = 35$ s-state. In this case, the turning points are $R_{\text{min}} \approx 1875$ a.u. and $R_{\text{max}} \approx 1970$ a.u.

In the framework of the conservative mean-field potential (2) this oscillation would continue until $t \rightarrow \infty$ and the energy of the ground state atom would not change, i.e. $\Delta E = 0$ (see blue dashed-dotted line in Fig. 1c). However, this situation is different in the quantum-classical treatment (see red solid line in Fig. 1c): With each oscillation, i.e. when $\mathbf{v}_{\text{Rb}} \neq 0$, energy is transferred to the Rydberg electron, and the ground state atom loses energy. The total detuning is on the order of ~ 0.02 kHz per oscillation and, thus, very small compared to the binding energy of several MHz. The detuning per oscillation therefore remains almost constant with time, and from averaging Eq. (8) we obtain a mean detuning over time [see Eq. (9)] on the order of $\langle dE/dt \rangle \sim 0.3$ kHz/ μ s.

3.2. Comparison with the experiment

In this section, we compare the time development of the detuning with the experimental investigations of the lifetimes. We again consider a Rydberg excitation of $n = 35$ which has also been investigated in detailed experimental lifetime measurements by Butscher *et al* [7].

Fig. 2 again shows the time development of the detuning (red solid line). The authors of Ref. [7] have measured the lifetimes of the $n = 35$ Rydberg state for different densities \mathcal{N} of the atomic background gas and found that the lifetime decreases with increasing density \mathcal{N} . Some of their results have been included in Fig. 2 for comparison (horizontal green dotted lines). As discussed in the introduction, they found a linear dependence of the decay rate on the density that indicates a $\tau_0 = 47.6$ μ s lifetime of the Rydberg molecule in the zero density limit (horizontal green dashed line, the horizontal green stripe indicates the experimental error). In contrast to the expectation that, in this limit, one would obtain the lifetime $\tau_{\text{atom}} = 62.5$ μ s of the bare atomic state (horizontal orange dotted line), the extrapolated value is still significantly reduced by about 25%.

To determine whether or not the detuning of the Rydberg state discussed above can play a role in reducing the lifetimes, we compare these two on the relevant time

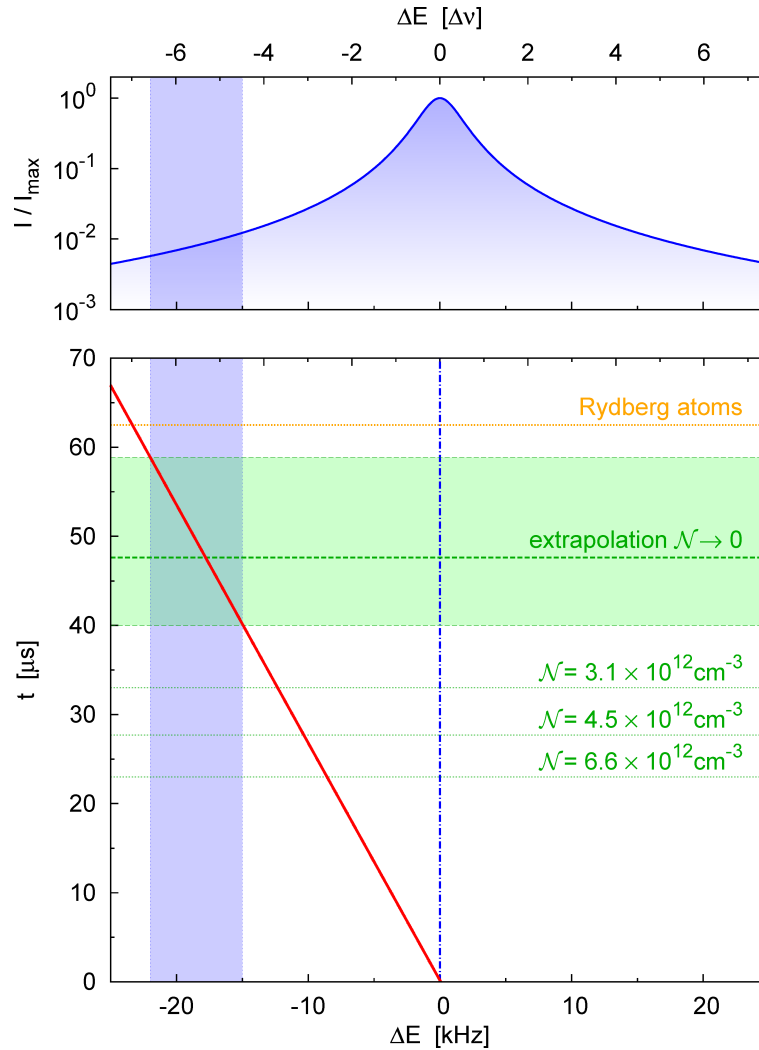


Figure 2. (Top) Lorentzian peak with a width $\Delta\nu$ corresponding to the lifetime of ^{87}Rb Rydberg molecules in the zero density limit. (Bottom) Development of the ground state atom's energy, ΔE (again, the Rydberg state is detuned by $-\Delta E$): Within the conservative mean-field description of the potential $V_s(\mathbf{R})$ in Eq. (2) the energy remains constant (blue dashed-dotted line), i.e. $\Delta E = 0$. By contrast, the quantum-classical model shows a permanent detuning (red solid line). For comparison the experimentally measured lifetimes of the Rydberg atoms and molecules are shown (horizontal dotted lines) for different densities \mathcal{N} as well as in the limit $\mathcal{N} \rightarrow 0$. The shaded areas indicate the experimental error (green horizontal stripe) and the region of the energy detuning which is present in this regime (blue vertical stripe). See text for further description.

scale. As can be seen in Fig. 2 the detuning of the Rydberg state reaches a value of $\Delta E \approx 15\text{--}22$ kHz (indicated by the vertical blue stripe) within the extrapolated lifetime including the experimental error. Comparing this detuning with the corresponding Lorentzian profile of the vibrational ground state which has a linewidth of $\Delta\nu = 3.4$ kHz (see top of Fig. 2), we obtain that this corresponds to a detuning of $\Delta E \approx (4.5\text{--}6.5)\Delta\nu$. This value is in accordance with the above estimated detuning where the quantum

mechanically “forbidden region” is reached, since for such a detuning the Lorentzian curve has decreased to $I/I_{\max} \lesssim 0.01$. The Rydberg wave function is then strongly detuned which can result in a significantly higher probability for its decay than one would expect from spontaneous decay or blackbody induced radiation. Therefore, we expect the lifetime of the Rydberg molecule to be determined by the time necessary for the detuning to significantly exceed the natural linewidth of the molecule.

As already discussed above, we also expect this strongly detuned Rydberg wave function to cause a change in the electronic structure (e.g. $n \rightarrow n - 1$) which, depending on the final state, may allow for different reactions, e.g. the dissociation of the Rydberg molecule. This picture is supported by the quantum mechanical interpretation of the process: In the case of a fixed ground state atom [9, 10], the scattering of a Rydberg electron will, in general, change its direction, but not its energy. This means that the scattering process does not conserve the angular momentum but the principal quantum number ($n = \text{const}$). However, in the case of a ground state atom with nonvanishing velocity ($\mathbf{v}_{\text{Rb}} \neq 0$), each scattering process causes a change of the Rydberg electron’s energy. For detunings which are small compared to the natural linewidth, this is possible within the linewidth of the respective Rydberg state n . Significant detunings on the order of the natural linewidth or even larger, however, are quantum mechanically related to couplings to other quantum states, i.e. the strongly detuned Rydberg state must, in general, be coupled to states with other principal quantum numbers n . The coupling can induce transitions to lower electronic states resulting in the decay of the molecule, as already discussed above.

3.3. Dependence on the principal quantum number

Detailed investigations of the lifetimes of Rydberg molecules can only be found for the $n = 35$ s-state in the literature so far [7]. However, already in the publication on their first experimental realisation [4], a dependence of the lifetime on the principal quantum number n has been discussed. Although these experiments have been performed at finite densities \mathcal{N} and an extrapolation to zero density is not possible due to the lack of data, the measured tendency of longer lifetimes with increasing quantum number n can also be expected to hold in the limit $\mathcal{N} \rightarrow 0$. We, therefore, present the behaviour of the Rydberg electron’s detuning for different n in the following.

In order to determine the detuning for different quantum numbers n , we proceed as done for the $n = 35$ state: We determine the molecular potential for the respective quantum number and place the point particle representing the ground state atom in the outermost well with an energy corresponding to the respective vibrational ground state. The average energy detuning $\langle dE/dt \rangle$ is calculated using Eq. (9).

Fig. 3 shows this mean energy detuning over time for different experimentally accessible quantum numbers $n = 33 - 41$ (red squares). The figure illustrates that the value $\langle dE/dt \rangle$ strongly depends on n showing a significant decrease of the detuning with an increasing quantum number. Two points contribute to this behaviour: (i) The

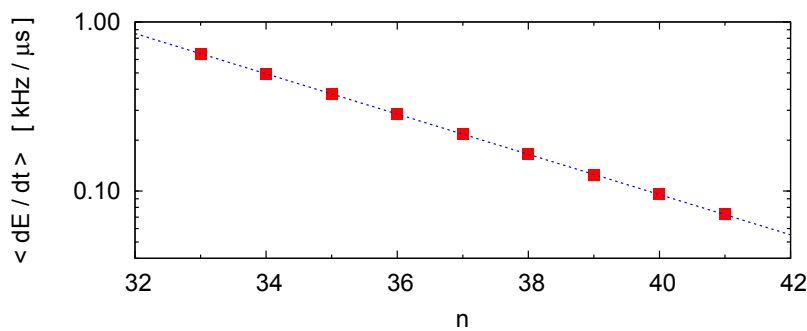


Figure 3. Dependence of the mean energy detuning over time $\langle dE/dt \rangle$ in Eq. (9) on the principal quantum number n . The calculations reveal a perfect exponential decrease of the detuning with the quantum number n .

extension of the Rydberg electron's wave function scales with $\langle r \rangle \sim n^2$ so that the atom becomes more extended with increasing n . At the same time the larger extension results in a smaller electron density $n_e^{(i)}$ at the position of the ground state atom, which lowers the effect of the finite mass correction term in Eq. (8). (ii) For higher principal quantum numbers, the outermost potential minimum becomes less deep so that the velocity of the ground state atom decreases. Because \mathbf{v}_{Rb} directly enters the correction term, its effect is further reduced.

For the decrease of the detuning with increasing n , we obtain a value of

$$(\Delta E/\Delta t)_n \sim 0.76^n \quad (11)$$

from Fig. 3. Assuming that – in analogy to the calculations for the $n = 35$ s-state – the decay of the Rydberg molecule was generally induced by the ground state atom when a detuning of $\Delta E \approx 15 - 22$ kHz is reached, this would mean an increase of the Rydberg molecule's lifetime by a factor of $1/0.76 \approx 1.32$. Note that, considering the experimental error stripes presented in Ref. [4], this value is in accordance with the lifetime measurements of the Rydberg molecules by Bendkowsky *et al* at finite densities [4].

4. Conclusion and outlook

We have investigated the vibrational ground state of Rydberg molecules within a quantum-classical treatment. In this model the dynamics of the ground state atom and the Rydberg electron are coupled, leading to a continuous energy transfer from the ground state atom to the Rydberg electron by which the Rydberg state is permanently detuned.

Comparing the time evolution of the detuning with these reduced lifetimes of the molecule, we observe that the measurements agree very well with the time at which the detuning significantly exceeds the natural linewidth. We, therefore, expect this detuning of the Rydberg state to give an important contribution to the reduced lifetimes

of Rydberg molecules. Also the experimentally measured tendency of longer lifetimes with higher Rydberg excitation could be verified within this model. However, further detailed experimental investigations of the corresponding lifetimes need to be performed for different densities of the background atomic gas as well as different quantum numbers n to verify the results also in the zero density limit of the atomic background gas. A fully quantum mechanical treatment of the process discussed in this paper and the accurate computation of the lifetimes are a challenge for future work.

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